Lyon and Rahn

The Function Of Time On The

Vitrification Of A Shale

# THE FUNCTION OF TIME ON THE VITRIFICATION OF A SHALE

BY

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AND
ROBERT CHARLES RAHN

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# THESIS

FOR THE

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IN

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

John Boyd Lyon and Robert Charles Rahn

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# THE FUNCTION OF TIME IN THE VITRIFICATION
# OF A SHALE.

## Introduction.

The term "vitrification", in the true sense, means the production of a glassy appearance, but it has been brought into the field of ceramics with a change in the true meaning. In reference to clays and ceramic bodies it is understood as an increase in density and the closing up of the pores due to the influence of heat. Two stages of vitrification must be recognized, viz., incipient, and complete vitrification. By incipient vitrification is meant the softening of a clay sufficiently to make the particles stick together, altho not enough to close all the pores. Complete vitrification signifies that the grains have softened to such an extent that all the pores are closed and the mass made impervious.

Up to, and including the period of oxidation, most clays show little, if any signs of vitrification. Upon further heating, with a rise in temperature minerals having the lowest melting-point begin to fuse. They in turn unite with the other minerals in a tendency to form compounds having lower melting-points than the combining minerals, with the result that a small mass of fused material is formed. These

minute masses of fused material, which are scattered thru the entire clay body begin to attack the surrounding mineral structure, with the final result that the grains become cemented with a silicious material. The minerals in fusing, which is a slow and steady process due to the extremely high viscosity of the silicates formed, tend to shape themselves into a sphere which represents their smallest volume. This reduction causes the particles to come closer together and results in a filling up of the pore space.

Vitrification, however, "is not entirely due to the action of fluxes. Part of it is undoubtedly to be ascribed to the contraction of the colloidal portions of the clays, since condensation is typical of many amorphous bodies such as pure alumina, magnesia, zirconia, etc. We have, however, no means of differentiating between the two kinds of contraction. In impure clays and materials like shales this condensation is not marked. The colloidal material causing the contraction in question is active in this direction only as long as it persists in the colloidal form."[1] The action ceases as the colloids become "set" by the action of heat, since the "setting" is a function of temperature.

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1.    Brown & Murray, Trans. Amer. Cer. Soc., Vol. 15.

The rapidity[2] with which the pores of a clay body will close up is dependent upon the kind, amount, and size of the fluxing minerals present, the homogeniety of the mass, the compounds formed, the condition of the fire, whether oxidizing or reducing, and the time and temperature of burning. For instance, in the case of very sandy clays, a small amount of fluxing minerals is present together with a large amount of sand which is coarse-grained and difficult to fuse. The burned ware of this clay is porous, due to the absence of enough fluxing material to form a fusible mass which will close the pores. If, on the other hand, there is present a large amount of fine grained minerals of high fluxing power together with a relatively small amount of refractory substance, there results too quick a fluxing action and the ware fuses and deforms at a rapid rate.

The size of mineral grains present in the clay has a marked effect on the fusibility of the latter. Fine grained clays, as a rule, fuse at lower temperatures than do coarse grained ones, due to the fact that the grains of the former come into more intimate contact with each other, thus raising the heat conductivity of the body. Furthermore, since the

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2.    Ries, H.,"Clays, Occurrence, Properties & Uses,"

fluxing action begins on the surface of the grains and works toward the center, those particles that are smallest will fuse most rapidly and will be more effective in their fluxing action than will the coarse grained ones.

Homogeniety of the mass affects the rate of vitrification insomuch that if the grains of each mineral are not uniformly distributed thruout the mass they cannot produce their maximum effect. When burning clays that contain an appreciable amount of iron oxide, the condition of the fire plays an important role in the fusion of the former. Ferrous iron, which is produced under reducing conditions has, according to Wheeler[3], a fusing point about 100°C. lower than ferric iron which is present under oxidizing conditions.

It has been shown, and is now universally conceded, that a certain temperature and heat treatment is required before any vitrification takes place. That a heterogeneous mixture can be made to fuse at a temperature below its normal fusing point by holding it at a lower temperature for a sufficient length of time, is shown in the use of cones. By a long period of heating, or "soaking", of these cones in a furnace or kiln, they can be made to bend over at a temperature as

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3. Ries, H.,"Clays, Occurrence, Properties & Uses." p. 85.

much as 100°C. below their rated temperature. This is due
to the fact that when once the fluxing action begins, it con-
tinues until the fusion of the particles is complete provi-
ding the temperature does not fall below the point where
this action takes place.

This at once suggests to the clayworker that he can
burn his ware to vitrification using a low temperature and a
long period of time or at a high temperature in a shorter
time. Burning the ware for a short period at a high temper-
ature results, in a downdraft kiln for instance, in the over-
burning of the top and the underburning of the bottom courses
of ware. If, on the other hand, an attempt is made to burn
the ware at too low a temperature in order that the heat may
get to the bottom before the top is overburned, considerable
time, labor, and fuel is used which might be saved. The ques-
tion then arises as to what heat treatment is best for the
particular clay to insure the best ware and at the same time
save labor and fuel.

The determination of the optimum temperature for burn-
ing ware to vitrification that is, the best treatment which
will permit the most efficient use of time and fuel without
danger of overburning and the production of vesicular struc-

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ture is of special importance in the manufacture of paving brick. In this ware, a vitrified product is required which shall have the maximum toughness. Any development of Fleb structure due to too high a heat treatment will result in a decreased toughness and is, therefore, undesirable.

Previous work on this subject has already been done by Bleininger and the Bureau of Standards. Their work was carried out with small pieces, burning them at constant rates of heating thru vitrification. The present work has been carried on with larger pieces, a longer firing period, and the use of constant temperatures during vitrification.

## METHOD OF PROCEDURE.

For this work, two Illinois shales commercially used for the manufacture of paving brick were selected, one from Galesburg, and the other from Streator. The shales, in lump form, were first ground in a dry pan; then tempered with water to stiff mud consistency in a wet pan. This material was run out thru a small auger machine into a cylindrical column $3\frac{1}{2}$" in diameter and was cut into blocks 2" thick. After drying in a steam-heated drier the pieces were oxidized at 750°C in a coal-fired kiln following the curve given in Figure I.

Figure I

Watersmoking
and
Oxidation Curve
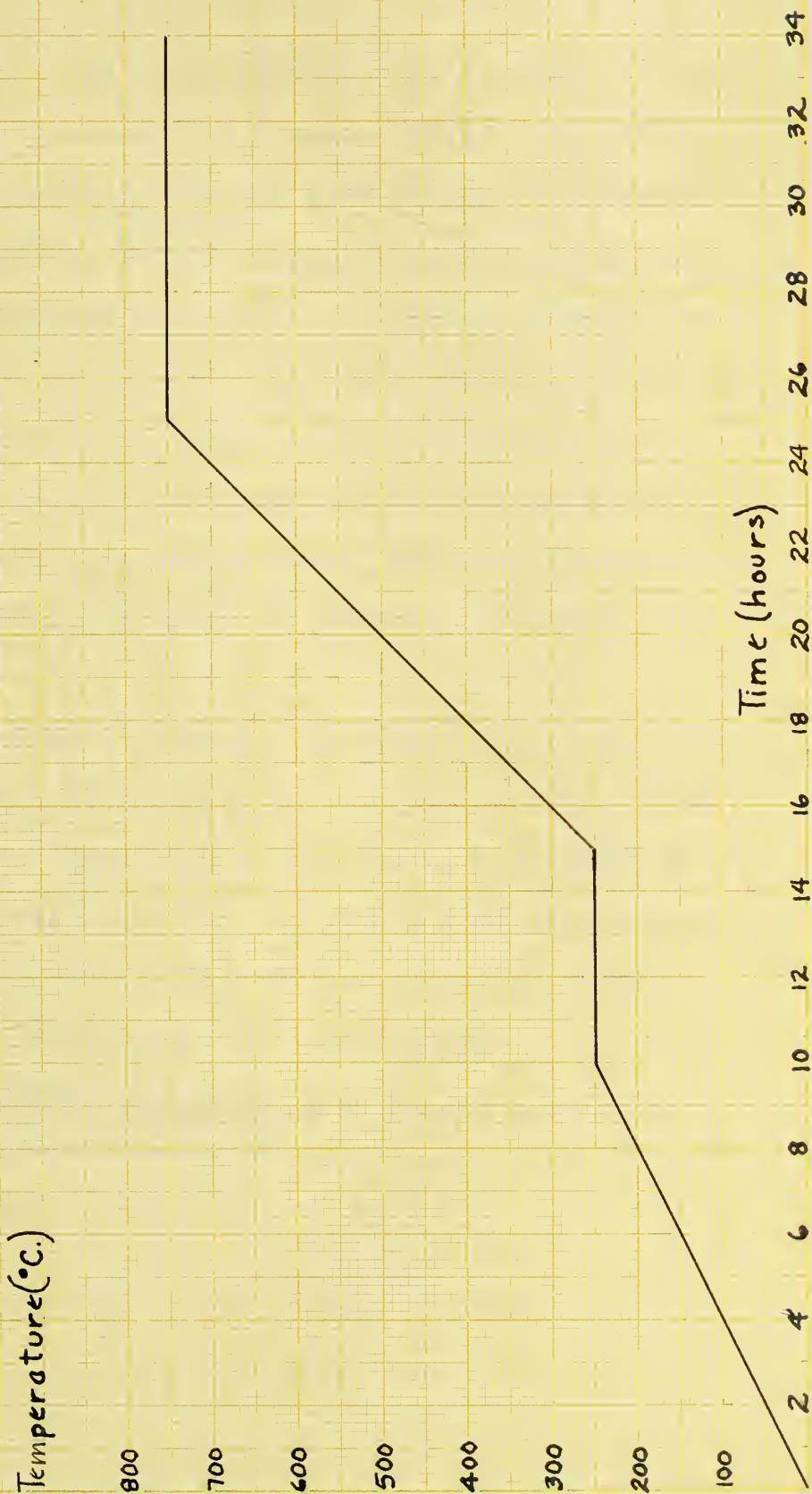
For the second, and final firing, perfect trial pieces were selected from the oxidized blocks. These were burned in a coal-fired kiln following the time-temperature curves in Figures II and III. In all cases, the same rate of heating was maintained up to the point at which the temperature was held constant. Oxidizing conditions, judged by the brightness of the interior of the kiln, were maintained throughout the firings. The temperature measurements were made with a platinum-platinum-rhodium thermocouple, the cold junction being kept at a constant temperature ($20^{o}C$) by immersion in a water bath.

Trials were drawn at regular intervals* after the desired temperature had been attained and the pieces were buried in sand until cool. Dry weights were taken; then wet and suspended weighings made after the pieces had been immersed in water in a cylinder under about 25" vacuum for 12 hours.

Porosity was calculated from the formula:-

$$\frac{\text{Wet weight - dry weight}}{\text{Wet weight - suspended weight}} \times 100 = \% \text{ porosity.}$$

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* See Figure III.

Time-Temperature
Burning Curves

Figure III

Figure II

Temperature (°C.)

## DATA.

### Galesburg Shale

### Table I.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1100°C | 0 | 3.52% )<br>3.98 )<br>*1.7 )<br>**---- ) | 3.75% |
| | 2 | .29 )<br>**---- )<br>.21 )<br>**---- ) | .25 |
| | 4 | .75 )<br>**---- )<br>.84 )<br>.328) | .64 |
| 1065°C | 0 | 18.1 )<br>18.3 )<br>13.25 )<br>*23.6 ) | 15.2<br>---- |
| | 2 | 6.0 )<br>5.81 )<br>7.12 )<br>* 6.38 ) | 5.94<br>---- |
| | 4 | 1.03 )<br>3.82 )<br>** ---- ) | 2.43<br>---- |
| | 6 | 2.09 )<br>** ---- )<br>1.41 )<br>2.18 ) | 1.9<br>--- |
| | 8 | 1.05 )<br>.51 )<br>.74 )<br>** ---- | .77<br>--- |

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*   Result not included in calculation of average porosity.
**  Trial Lost.

Table I. Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1065°C | 10 | .71 )<br>.36 )<br>.82 )<br>.75 ) | .68<br>--- |
| | 12 | .17 )<br>.39 )<br>.83 )<br>.0 ) | .35<br>--- |
| | 14 | .0 )<br>.25 )<br>.13 )<br>.47 ) | .21<br>--- |
| 1050°C | 0 | 24.6 )<br>22.8 )<br>23.1 )<br>22.6 ) | 23.3<br>---- |
| | 2 | 6.8 )<br>6.59 )<br>7.36 )<br>* 7.48 ) | 6.80<br>---- |
| | 4 | 5.64 )<br>8.17 )<br>3.06 )<br>5.64 ) | 5.85<br>---- |
| | 6 | * 8.49 )<br>4.16 )<br>** ---- )<br>4.42 ) | 4.3<br>--- |
| | 8 | 3.28 )<br>** ---- )<br>5.36 )<br>3.02 ) | 3.55<br>---- |

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*   Results not included in calculation of average porosity.
**  Trial Lost.

Table I. Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1025° | 22 | 3.67 )<br>** ____ )<br>3.68 )<br>3.48 ) | 3.61 |
| | 25 | 5.1 )<br>7.14 )<br>7.65 )<br>* 14.8 ) | 6.63 |
| 1050°C | 0 | 25 )<br>22.85 )<br>29.8 )<br>28.7 ) | 26.54 |
| | 4 | 33.6 )<br>19.1 )<br>** ____ )<br>** ____ ) | 21.5 |
| | 8 | 14.9 )<br>15.3 )<br>* 21.8 )<br>17.4 ) | 15.9 |
| | 12 | , 4.31 )<br>6.89 )<br>** ____ )<br>** ____ ) | 5.6 |
| | 16 | 4.43 )<br>2.47 )<br>2.93 )<br>3.73 ) | 3.39 |
| | 20 | 2.22 )<br>3.23 )<br>* .71 )<br>1.05 ) | 1.80 |

---
\*     Result not included in calculation of average porosity.
\*\*   Trial Lost.

Table I. Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1025°C | 0 | 19.4 )<br>19.1 )<br>20.33 )<br>18.75 ) | 19.39 |
| | 7 | 8.7 )<br>9.43 )<br>*4.1 )<br>**---- ) | 9.56 |
| | 9 | 3.26 )<br>**---- )<br>4.19 )<br>4.14 ) | 3.86 |
| | 11 | 2.35 )<br>1.83 )<br>.94 )<br>2.04 ) | 1.79 |
| | 13 | 4.42 )<br>4.46 )<br>1.29 )<br>2.19 ) | 3.09 |
| | 15 | 2.32 )<br>1.83 )<br>**---- )<br>*0.46 ) | 2.07 |
| | 17 | 4.1 )<br>1.72 )<br>3.12 )<br>3.3 ) | 3.06 |
| | 19 | *.585)<br>**----)<br>4.14)<br>4.98) | 4.52 |

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\*    Result not included in calculation of average porosity.
\*\*   Trial Lost.

Table I. Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1050°C | 24 | 1.01 )<br>.8 )<br>1.34 )<br>1.18 ) | 1.08 |
| | 28 | .87 )<br>.92 )<br>1.47 )<br>** ---- ) | 1.09 |
| | 34 | ** ---- )<br>.79 )<br>1.47 )<br>1.08 ) | 1.11 |
| | 38½ | .77 )<br>.92 )<br>** --- )<br>** --- ) | .85 |
| | 42 | .3 )<br>.21 )<br>.48 )<br>.27 ) | .32 |

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**   Trial Lost.

Streator Shale.

Table II.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1100°C | 0 | 3.60 )<br>** ---- )<br>3.21 )<br>3.72 ) | .18 |
| | 2 | 2.03 )<br>1.82 )<br>3.34 )<br>2.55 ) | .11 |
| | 4 | * 3.17 )<br>2.00 )<br>2.02 )<br>2.05 ) | .04 |
| 1065°C | 0 | 14.92 )<br>17.85 )<br>15.6 )<br>14.7 ) | 15.32 |
| | 2 | 6.73 )<br>6.9 )<br>7.5 )<br>** ---- ) | 7.04 |
| | 4 | 3.83 )<br>2.57 )<br>3.92 )<br>* 1.85 ) | 3.81 |
| | 6 | 4.15 )<br>1.17 )<br>5.13 )<br>3.93 ) | 4.4 |

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*    Result not included in calculation of average porosity.
**   Trial Lost.

Table II, Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1065°C | 8 | 3.91 )<br>3.68 )<br>3.12 )<br>2.19 ) | 2.95 |
| | 10 | 3.12 )<br>2.25 )<br>2.06 )<br>**---- ) | 2.14 |
| | 12 | 1.99 )<br>1.66 )<br>1.81 )<br>1.69 ) | 1.79 |
| | 14 | 1.63 )<br>*2.09 )<br>1.43 )<br>1.65 ) | 1.57 |
| 1050°C | 2 | 10.50 )<br>10.75 )<br>11.38 )<br>*12.9 ) | 10.88 |
| | 4 | 8.45 )<br>8.68 )<br>3.30 )<br>9.55 ) | 8.99 |
| | 6 | 8.08 )<br>8.66 )<br>9.60 )<br>*11.5 ) | 9.08 |
| | 8 | 9.2 )<br>8.96 )<br>8.43 )<br>9.05 ) | 8.91 |

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*  Result not included in calculation of average porosity.
** Trial Lost.

Table II. Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1025°C | 0 | 20.1 )<br>19.6 )<br>21.2 )<br>21.2 ) | 20.5 |
| | 7 | 11.3 )<br>10.7 )<br>10.87)<br>9.60) | 10.37 |
| | 9 | 10.92)<br>11.02)<br>9.97)<br>10.6 ) | 10.38 |
| | 11 | 10.0 )<br>9.9 )<br>**____ )<br>9.04) | 9.65 |
| | 13 | 7.93)<br>11.1 )<br>9.05)<br>8.96) | 9.51 |
| | 15 | 7.5 )<br>8.59)<br>6.9 )<br>*12.05) | 7.0 |
| | 17 | 9.72)<br>7.2 )<br>8.75)<br>9.03) | 8.7 |
| | 19 | 7.77)<br>7.71)<br>7.9 )<br>*9.17) | 7.79 |

--------------------------------
\*  Result not included in calculation of average porosity.
\*\* Trial Lost.

Table II. Con.

| Temperature | Time (Hr.) | | Porosity | Av. Por. |
|---|---|---|---|---|
| 1025°C | | | 8.26 ) | |
| | 22 | | 8.52 ) | |
| | | | 8.00 ) | 8.04 |
| | | | 7.36 ) | |
| | 25 | ** | 10.5 ) | |
| | | ** | ---- ) | |
| | | | ---- ) | 9.67 |
| | | | 8.85 ) | |
| 1050°C | | | 29.5 ) | |
| | 0 | | 28.75 ) | |
| | | | 27.65 ) | 28.67 |
| | | | 28.8 ) | |
| | 4 | | 17.4 ) | |
| | | | 18.45 ) | |
| | | * | 21.35 ) | 18.77 |
| | | | 17.9 ) | |
| | 8 | | 14.9 ) | |
| | | | 16.85 ) | |
| | | | 15.2 ) | 16.18 |
| | | * | 17.9 ) | |
| | 12 | | 11.83 ) | |
| | | | 10.65 ) | |
| | | | 9.72 ) | 10.6 |
| | | | 10.3 ) | |
| | 16 | | 7.6 ) | |
| | | | 7.8 ) | |
| | | | 9.22 ) | 7.52 |
| | | | 6.46 ) | |
| | 20 | ** | ---- ) | |
| | | | 5.51 ) | |
| | | | 5.81 ) | 5.93 |
| | | | 6.46 ) | |
| | 24 | | 6.25 ) | |
| | | | 5.60 ) | |
| | | | 5.27 ) | 5.28 |
| | | | 4.93 ) | |

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* Result not included in calculation of average porosity.
** Trial Lost.

Table II Con.

| Temperature | Time (Hrs.) | Porosity | Av. Por. |
|---|---|---|---|
| 1050°C | | 3.53 ) | |
| | 28 | 2.69 ) | |
| | | 4.31 ) | 3.73 |
| | | 3.59 ) | |
| | 34 | 3.77 ) | |
| | | 3.82 ) | |
| | | 3.59 ) | 3.58 |
| | | 3.15 ) | |
| | 38½ | 3.62 ) | |
| | | 3.41 ) | |
| | | **----  ) | 3.03 |
| | | 1.95 ) | |
| | 42 | 3.5  ) | |
| | | 4.14 ) | |
| | | 1.06 ) | 2.44 |
| | | 1.05 ) | |

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\*   Results not included in calculation of average porosity.
\*\*  Trial Lost.

## RESULTS.
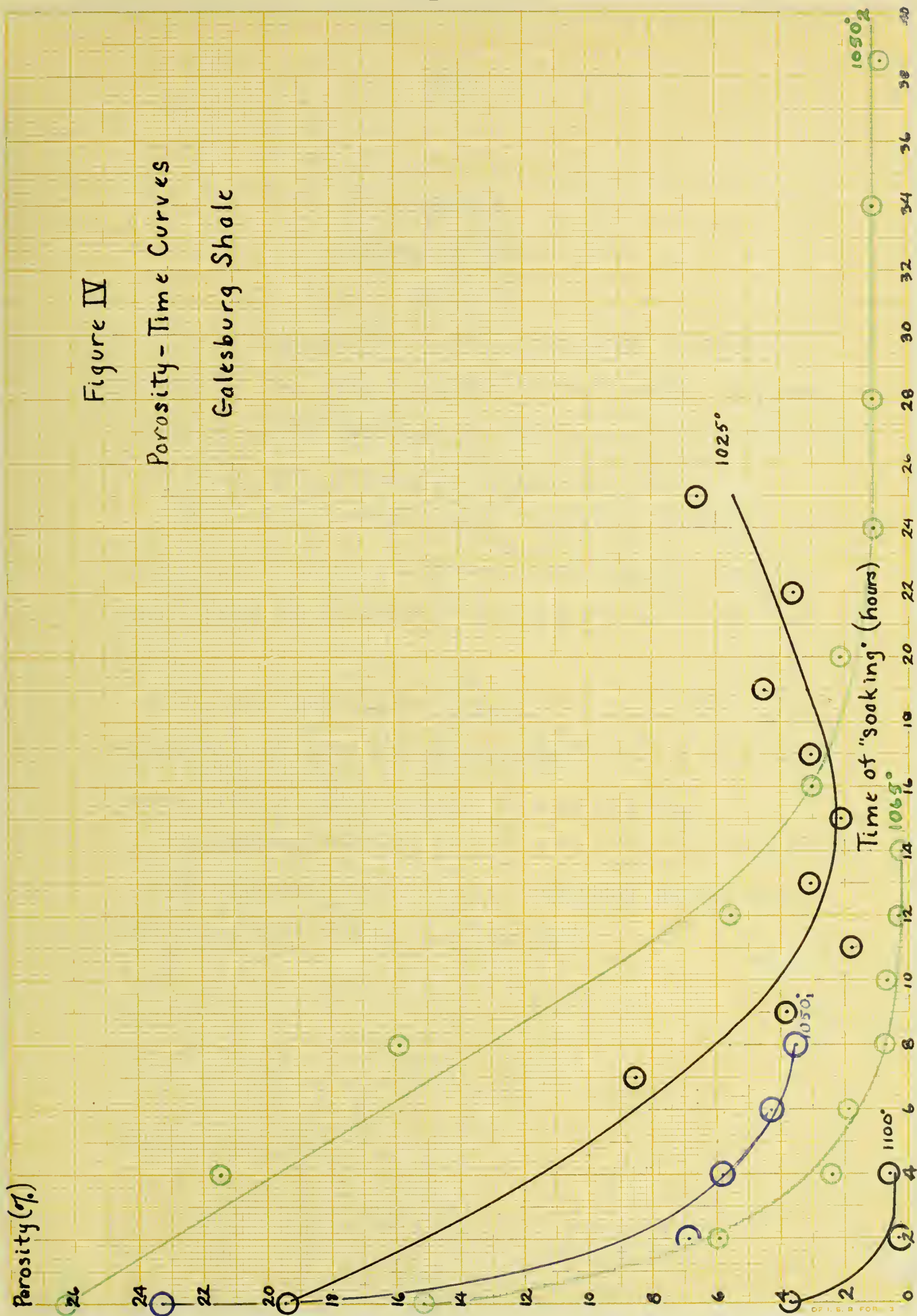
### Galesburg Shale

### Table I.

The average porosities given in the above table are shown in Figure 4. The results of the 1025° burn vary rather widely toward the end of the period of heating, due probably to alternate oxidation and reducing conditions, in the kiln, and no special significance is attached to the fact that the curve rises. The lack of careful regulation of the firing was probably the cause of the non-uniformity of gas conditions during this burn.

The shorter 1050° curve suggests a safe drop to a low porosity and a subsequent burn at the same temperature shows the action of that heat treatment. The slow decrease to a low porosity and a continuance of such conditions are very desirable.

At 1065° and 1100°, the drop in porosity is more rapid than for the lower temperatures and the very low porosities suggest that a slightly longer period of heating would have caused overburning, with development of vesicular structure and a rise in the porosity curve.

Figure IV

Porosity–Time Curves

Galesburg Shale

## RESULTS.

### Streator Shale,

### Table II.

As in Fig. 4, the curve for the 1025° burn shows a tendency to rise toward the end of the period. The same suggestion may be made here as in the case of the Galesburg shale,--lack of uniformly oxidizing conditions.

The original 1050° firing suggests a dangerous decrease in porosity, but the latter one shows a rather slow drop without reaching a constant low porosity, as is the case in Fig. 4.

For the 1065° heat treatment the curve dips rapidly to a desirable porosity and it is probable that a considerably longer period of heating might be safely used.

The sudden decrease in porosity at 1100° indicates that a longer treatment would result in overburning. The short range makes this temperature unsafe.

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Figure V

Porosity–Time Curves

Streator Shale
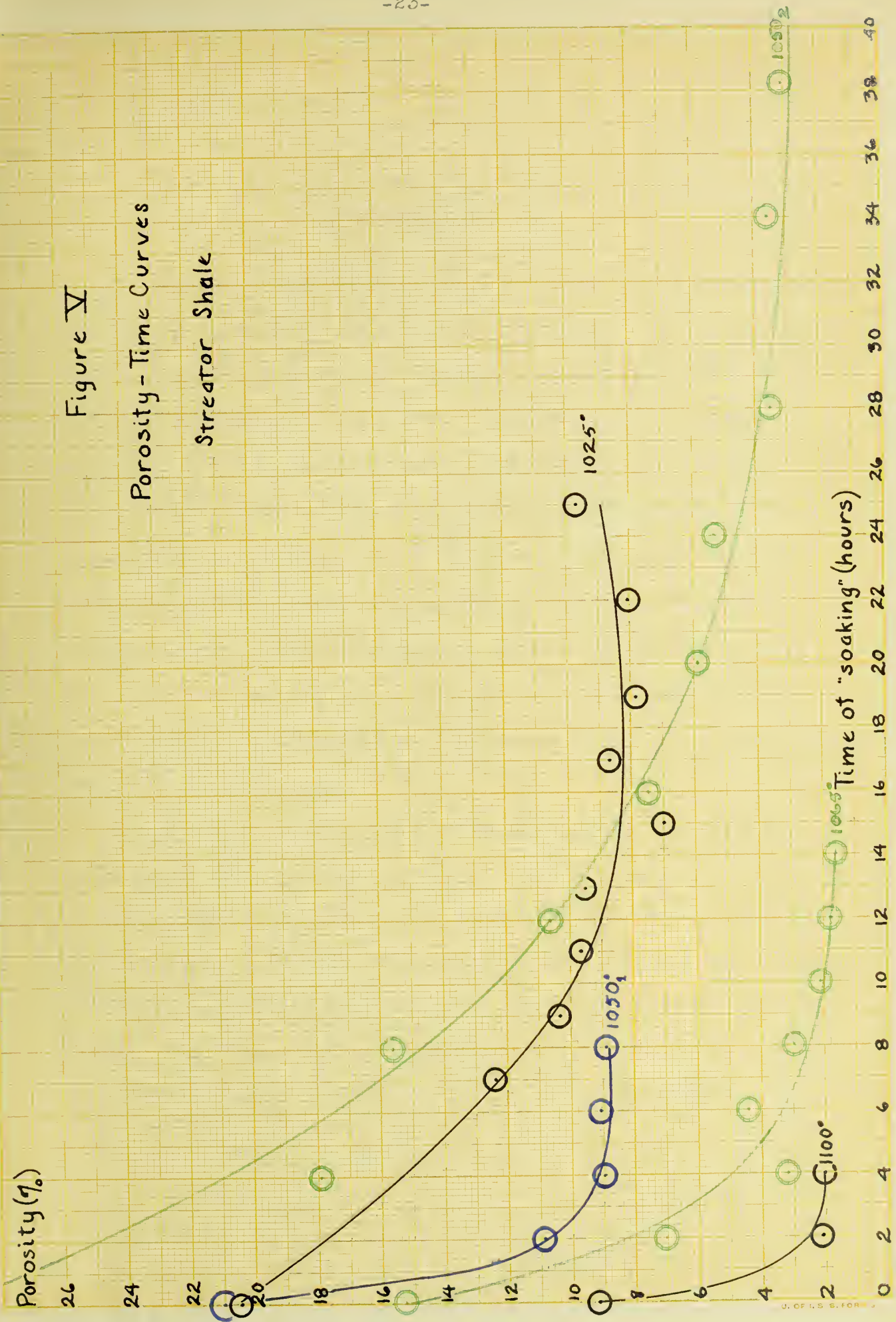
## CONCLUSIONS

The results shown in Figures 4 & 5 make plain the effect
of varying time and temperature on porosity. It will be noted
that low porosities may be obtained in two ways, viz., with a
low temperature and a long period of heating, or a higher
temperature for a shorter time. This relation, however, holds
only within narrow limits near the optimum temperature, that
temperature at which porosity decreases at a moderate rate
and holds constant over a long period of time. For the
shales tested, a temperature much higher allows but a very
short time range, and for a temperature much lower, either
the time will be so long as to be impractical or no vitrifica-
tion will be obtained.

A comparison of the two shales shows that the Streator
shale requires a greater degree of heat treatment than the
Galesburg shale to develop the same degree of vitrification.
In all cases, the porosity of the blocks of Galesburg shale was
lower for a given temperature than for those made of Streator
shale. The best burning temperature for the Galesburg shale
is probably 1050°, and for the Streator shale, 1060°.